

## NICKEL-CONTAINING ALLOYS, METHOD OF MANUFACTURE THEREOF AND ARTICLES DERIVED THEREFROM

### BACKGROUND

[0001] This disclosure is related to nickel-containing alloys, methods of manufacture thereof and the articles derived therefrom.

[0002] High temperature alloys suitable for use in turbine nozzle and airfoil applications generally display high temperature strength, corrosion resistance, and properties such as castability and weldability. Unfortunately, the process of optimizing one property generally results in the reduction of another. The process of alloy design generally results in compromises to achieve the best overall mix of properties to satisfy the various requirements of component design. In such a design process, rarely is any one property maximized. Rather, through development of a balanced chemistry and proper heat treatment, the best compromise among the desired properties is achieved.

[0003] Cobalt containing alloys are found to be used for first stage turbine nozzle applications despite their susceptibility to thermal fatigue cracking. The reason for the acceptance of these alloys is the ease with which they can be repair welded. However, in latter stage nozzles, cobalt-based alloys have been found to be creep limited to the point where downstream creep of the nozzles can result in unacceptable reductions of turbine diaphragm clearances. Although cobalt-based alloys with adequate creep strength for these latter stage nozzle applications are available, they do not possess the desired weldability characteristics. It is therefore desirable to find other alloys that display creep resistance, hot corrosion resistance, castability and weldability, and that can be used in first stage and later stage turbine nozzle applications.

### BRIEF DESCRIPTION OF THE INVENTION

[0004] Disclosed herein is a nickel-containing alloy comprising about 1.5 to about 4.5 weight percent aluminum; about 1.5 to about 4.5 weight percent titanium;

up to about 3 weight percent niobium; about 14 to about 28 weight percent chromium; with the remainder being nickel.

[0005] Disclosed herein is a nickel-containing alloy comprising about 1.6 to about 1.8 weight percent aluminum; about 2.2 to about 2.4 weight percent titanium; about 1.25 to 1.45 weight percent niobium; about 22 to about 23 weight percent chromium; about 18.5 to about 19.5 weight percent cobalt; about 0.08 to about 0.12 weight percent carbon; about 1.9 to about 2.1 weight percent tungsten; and about 0.002 to about 0.006 weight percent boron; up to 0.01 weight percent zirconium; with the remainder being nickel.

[0006] Disclosed herein is a method for manufacturing an article comprising casting an alloy comprising about 1.5 to about 4.5 weight percent aluminum; about 1.5 to about 4.5 weight percent titanium; up to about 3 weight percent niobium; about 14 to about 28 weight percent chromium; about 10 to 23 weight percent cobalt; about 1 to about 3 weight percent of tungsten, rhenium, ruthenium, molybdenum, or a combination thereof; about 0.02 to about 0.15 weight percent of carbon; about 0.001 to about 0.025 weight percent of boron; up to 0.2 weight percent of zirconium, hafnium, or a combination thereof; into a mold; and solidifying the casting

[0007] Disclosed herein too are articles derived from the aforementioned compositions.

#### BRIEF DESCRIPTION OF THE DRAWING

[0008] The figure is graphical representation of the strain versus time for two samples subjected to a constant stress of 15 ksi at a temperature of 871°C.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] Disclosed herein is a nickel-containing alloy for use in turbine applications. The nickel-containing alloy can advantageously be used for both first stage and later stage turbine nozzle applications as well as for use in large buckets for turbines. The nickel-containing alloy comprises nickel, chromium, cobalt, tungsten, aluminum, titanium, niobium, and other necessary elements. In particular, the nickel-

containing alloy has unique combination of concentrations of aluminum and titanium when compared with other similar alloys. This results in a decrease or elimination of the presence of undesirable phases such as the eta ( $\eta$ ) phase with an hexagonal crystal structure and a formula of  $M_3Ti$ , where M is nickel or an alloy of nickel, such as nickel-cobalt, and the like. This decrease in the  $\eta$  phase, promotes an increase in the creep resistance, as well as renders the alloy metallurgically stable at high temperatures, e.g., above 600 C.

[0010] The nickel-containing alloy comprises primarily nickel alloyed with chromium, titanium, aluminum, and niobium. Optional metals that may be added to the nickel-containing alloy are cobalt, carbon, zirconia, tungsten, boron, tantalum, hafnium, rhenium, ruthenium, molybdenum, or a combination comprising at least one of the foregoing metals.

[0011] In one embodiment, the nickel-containing alloy comprises aluminum and titanium in an amount of about 2 to about 9 weight percent (wt.%), of the nickel-containing alloy. Within this range, an amount of aluminum combined with titanium of greater than or equal to about 2.5 wt.%, preferably greater than or equal to about 3.0 wt.%, and more preferably greater than or equal to about 4 wt.% of the nickel-containing alloy may be used. Also desirable within this range, are amounts of less than or equal to about 8.8, preferably less than or equal to about 8.6, and more preferably less than or equal to about 8.0 wt.% of the nickel-containing alloy.

[0012] The aluminum content in the nickel-containing alloy is about 1.5 to about 4.5 wt.% of the nickel-containing alloy. Preferred values of aluminum are greater than or equal to about 1.6, with greater than or equal to about 1.7 more preferred. Preferred values of aluminum are less than or equal to about 4.00, with less than or equal to about 3 more preferred, and less than or equal to about 2.5 wt.% even more preferred. The titanium content in the nickel-containing alloy is about 1.5 to about 4.5 wt.%, of the nickel-containing alloy. Preferred values of titanium are greater than or equal to about 1.65, with greater than or equal to about 2 more preferred, and greater than or equal to about 2.25 wt.% even more preferred. Preferred values of titanium are less than or equal to about 4, with less than or equal

to about 3.5 more preferred, and less than or equal to about 3 wt.% even more preferred.

[0013] In general it is desirable for the atomic ratio of aluminum to titanium in the nickel-containing alloy to be about 0.2 to about 1.5. An aluminum to titanium atomic ratio within this range generally permits the improvement of hot corrosion resistance, weldability, and castability. Other aluminum to titanium atomic ratios that may be utilized within this range are greater than or equal to about 0.3, preferably greater than or equal to about 0.4, and more preferably greater than or equal to about 0.5. Also desirable within this range, are aluminum to titanium atomic ratios of less than or equal to about 1.4, preferably less than or equal to about 1.3, and more preferably less than or equal to about 1.2.

[0014] In another embodiment, it is desirable to control the sum of aluminum, titanium, and niobium present in the nickel-containing alloy to an amount of about 2 to about 13 weight percent effective to maintain the gamma-prime ( $\gamma'$ ) phase. A preferred value for the  $\gamma'$  phase is 15 to 45 volume percent. Strength in high temperature nickel-containing alloys generally derives from several different mechanisms such as the precipitation strengthening of a  $\gamma'$  phase, solid solution strengthening and carbide strengthening at grain boundaries. The ( $\gamma'$ ) phase consists of  $[\text{Ni}_3(\text{Al}, \text{Ti})]$ . Of these, precipitation strengthening of the  $\gamma'$  phase is the primary strengthening mechanism for the nickel-containing alloys.

[0015] In order to attain the best compromise among alloy properties for gas turbine nozzle and airfoil applications, the content of the primary precipitation-strengthening elements, i.e., titanium, aluminum, and niobium is maintained in an amount of about 2 to about 12 wt.%, of the nickel-containing alloy. Within this range, it is generally desirable to have an amount of titanium, aluminum and niobium greater than or equal to about 4.35, preferably greater than or equal to about 4.5, and more preferably greater than or equal to about 4.75 wt.%, of the nickel-containing alloy. Also desirable within this range, are amounts of less than or equal to about 11.5, preferably less than or equal to about 11, and more preferably less than or equal to about 10 wt.%, of the nickel-containing alloy. By maintaining the amount of

aluminum, titanium and niobium within the aforementioned limits, a good balance between creep resistance and weldability properties is achieved. In addition, the levels of carbon and zirconium have been carefully balanced and controlled to increase the castability of the nickel-containing alloy.

[0016] In another embodiment, the nickel-containing alloy is devoid of tantalum. It is generally desirable to have the niobium present in an amount of up to about 3 wt.%, of the nickel-containing alloy. Within this range, amounts of less than or equal to about 2.5, preferably less than or equal to about 2.0, and more preferably less than or equal to about 1.75 wt.% may be used. An exemplary value of niobium is about 1.35 wt.% of the nickel-containing alloy.

[0017] Chromium is generally present in an amount of about 14 to about 28 wt.%, of the nickel-containing alloy. Within this range, it is generally desirable to use the chromium in amounts of greater than or equal to about 16, preferably greater than or equal to about 17, and more preferably greater than or equal to about 20 wt.%, of the nickel-containing alloy. Also desirable within this range, is an amount of less than or equal to about 27, preferably less than or equal to about 26, and more preferably less than or equal to about 25 wt.%, of the nickel-containing alloy. An exemplary amount of chromium is about 22 to about 23 wt.% of the total nickel-containing alloy.

[0018] The nickel comprises the remaining weight percent of the nickel-containing alloy. The nickel is present in an amount of about 40 to about 70 wt.%, of the nickel-containing alloy. Within this range, it is generally desirable to use the nickel in amounts of greater than or equal to about 43, preferably greater than or equal to about 44, and more preferably greater than or equal to about 46 wt.%, of the nickel-containing alloy. Also desirable within this range, is an amount of less than or equal to about 65, preferably less than or equal to about 60, and more preferably less than or equal to about 55 wt.%, of the nickel-containing alloy. An exemplary amount of nickel is about 45 to about 55 wt.% of the nickel-containing alloy.

[0019] As stated above, optional metals that may be added to the nickel-containing alloy are cobalt, carbon, tungsten, zirconium and boron. Cobalt is

generally added in amounts of about 10 to about 24 wt.%, of the total nickel-containing alloy. Within this range, amounts of greater than or equal to about 14, preferably greater than or equal to about 15, and more preferably greater than or equal to about 17 wt.%, of the nickel-containing alloy may be used. Also desirable for use within this range are amounts of less than or equal to about 23.5, preferably less than or equal to about 22.5, and more preferably less than or equal to about 21 wt.%, of the total nickel-containing alloy. An exemplary amount of cobalt is about 18.5 to about 19.5 wt.% of the total nickel-containing alloy.

[0020] Carbon is generally added in amounts of less than 0.15 wt.%. A preferred amount of carbon is 0.02 to about 0.15 wt%. The carbon generally alloys with metals like titanium, tungsten and the like to form monocarbides. Generally the titanium and/or the tungsten in the monocarbide constitutes an amount of less than or equal to about 80 wt.% of the carbide phase. An exemplary amount of carbon is about 0.02 to about 0.15 wt.%, of the nickel-containing alloy.

[0021] Tungsten may be present in amounts of less than or equal to about 3 wt.%, of the nickel-containing alloy. The tungsten may be substituted by molybdenum, rhenium, ruthenium, and the like if desired. An exemplary amount of tungsten is about 1.9 to about 2.1 wt.%, of the nickel-containing alloy.

[0022] Boron may also be present in amounts of less than or equal to about 0.025 wt.%, of the nickel-containing alloy. A preferred amount of boron is about 0.001 to about 0.025 wt% of the nickel-containing alloy. The boron generally reacts with the metals in the nickel-containing alloy to form metal borides. An exemplary amount of boron in the nickel-containing alloy is about 0.002 to about 0.006 wt.%, of the nickel-containing alloy.

[0023] Zirconium may also added in amounts of less than or equal to about 0.2 wt.%, of the nickel-containing alloy. Zirconium may be substituted with hafnium if desired. An exemplary amount of zirconium is about 0.01 wt.%, of the nickel-containing alloy.

[0024] The nickel-containing alloy may be processed in one of several existing methods to form components for a gas turbine. Examples of such components include rotating buckets (or blades), non-rotating nozzles (or vanes), shrouds, combustors, and the like. Preferred components for utilizing the nickel-containing alloy are nozzles and buckets in gas turbines. The turbine components may be formed by a variety of different processes such as, but not limited to, powder metallurgy processes (e.g., sintering, hot pressing, hot isostatic processing, hot vacuum compaction, and the like), ingot casting followed by directional solidification, investment casting, ingot casting followed by thermo-mechanical treatment, near-net-shape casting, chemical vapor deposition, physical vapor deposition, and the like. Preferred processes are ingot casting followed by directional solidification and investment casting.

[0025] In one embodiment, in one manner of manufacturing a gas turbine airfoil from the nickel-containing alloy, the components of the nickel-containing alloy in the form of a powder, particulates, or the like, are heated to a temperature of about 1350 to about 1750°C, to melt the metal components.

[0026] The molten metal may then be poured into a mold in a casting process to produce the desired shape. The casting process may involve investment casting, ingot casting, or the like. Investment casting is generally used to make parts that cannot be produced by normal manufacturing techniques, such as turbine buckets that have complex shapes, or turbine components that have to withstand high temperatures. The mold is made by making a pattern using wax or another material that can be melted away. This wax pattern is dipped in refractory slurry, which coats the wax pattern and forms a skin. This is dried and the process of dipping in the slurry and drying is repeated until a robust thickness is achieved. After this, the entire pattern is placed in an oven and the wax is melted away. This leads to a mold that can be filled with the molten nickel-containing alloy. Because the mold is formed around a one-piece pattern, (which does not have to be pulled out from the mold as in a traditional sand casting process), very intricate parts and undercuts can be made. The wax pattern itself is made by duplicating using a stereo lithography or similar model-which has been fabricated using a computer solid model master.

[0027] Just before the pour, the mold is pre-heated to about 1000°C to remove any residues of wax as well as to harden the binder. The pour in the pre-heated mold also ensures that the mold will fill completely. Pouring can be done using gravity, pressure, inert gas, or vacuum conditions. The preferred embodiment is to cast in vacuum. In another embodiment, ingot casting may be used to form the turbine components. After the casting, the melt in the mold is directionally solidified. Directional solidification generally results in elongated grains in the direction of growth, thus higher creep strength for the airfoil than an equiaxed cast. The cost of directional solidification is higher than that of the equiaxed casting. Depending on the specified requirements of the airfoil, it can be either equiaxed or directional solidified. Following directional and/or equiaxed solidification, the castings are air cooled.

[0028] The castings comprising the nickel-containing alloy may then optionally be subjected to different heat treatments in order to optimize the strength as well as to increase creep resistance. In one embodiment, the casting is heat treated at temperatures of about 1095°C to about 1200°C to optimize the yield strength and to reduce creep resistance. This heat treatment is generally conducted for a time period of about 1 to about 6 hours. The preferred time period for the heat treatment is 4 hours. In another embodiment, a heat treatment cycle may be used to reduce the creep resistance. The cycle comprises heating the casting to a temperature of about 1150°C for 4 hours, followed by 1000°C for 6 hours, followed by 900°C for 24 hours, and concluding with 700°C for 16 hours. This heat treatment yields significantly improved values of tensile strength and yield strength.

[0029] In yet another embodiment, the material is solution heat treated at a temperature of 750°C to about 850°C. The solution treatment is generally carried out for a time period of about 8 to about 36 hours. An exemplary time period is about 24 hours. In general, the heat treatment and the solution heat treatment is used to reduce the presence of any undesirable phases such as the  $\eta$  phase.

[0030] The casting may optionally be subjected to hot isostatic pressing (HIP). The hot isostatic pressing is generally preferred for its ability to facilitate substantially reduced porosity and reduced shrinkage in the production of such components.



Generally, process conditions for hot isostatic pressing are chosen so as to achieve consolidation wherein the final composite has a porosity less than or equal to about 10 volume percent, and more preferably less than or equal to about 2 volume percent, based on the total volume of the composite article. This process generally involves the application of high pressure and temperatures through the medium of a pressurizing gas to remove internal porosity and voids, thus increasing density and improving the properties of the resultant composite. Hot isostatic pressing is generally conducted at temperatures of greater than or equal to about 1000°C, preferably greater than or equal to about 1050°C, more preferably greater than or equal to about 1150°C. The gas pressures utilized during hot isostatic pressing are generally greater than or equal to about 100 mega Pascals (MPa), preferably greater than or equal to about 150 MPa, and more preferably greater than or equal to about 200 MPa. Preferred gases used for the process include, but are not limited to, argon, nitrogen, helium, xenon and combinations comprising one of the foregoing.

[0031] As stated above, the nickel-containing alloys may be advantageously used for large airfoils in large turbines. The reduction in the undesirable phases such as the  $\eta$  phase and an increase in the volume fraction of the  $\gamma'$  phase to about 15 to 45 volume percent of the nickel-containing alloy, permit the nickel-containing alloy to show improved creep resistance, high temperature corrosion resistance and improved castability and weldability.

[0032] The following examples, which are meant to be exemplary, not limiting, illustrate compositions and methods of manufacturing some of the various embodiments of the nickel-containing alloy using various materials and apparatus.

#### EXAMPLE

[0033] This example was undertaken to demonstrate the improvement in properties of a nickel-containing alloy that does not contain any tantalum versus a comparative nickel-containing alloy sample containing tantalum. The samples having the comparative composition as well as those embodying the present modification are shown in Table 1. From the table, it may be seen that the comparative sample

(sample #1) has tantalum, whereas the other samples (samples #2 - 6) do not possess tantalum.

[0034] The samples were prepared by taking the various components of the samples shown in the Table 1 and heating them to temperature of 1550°C, to create a melt which was then cast. The samples were air cooled. The samples were annealed at 1150 °C for 4 hours and aged at 780 °C for 24 hours. The samples were subjected to creep testing in a tensile testing machine at a temperature of 1600°F, under a stress of 15 kilograms per square inch (Ksi). The time taken to reach a strain of 1% was measured and recorded as a function of the samples ability to display creep resistance. The sample is a cylindrical dog-bone type standard creep sample with a total length of 4 inches and the gauge diameter of about 0.25 inch.

Table 1

Sample #	Carbon (wt%)	Chromium (wt%)	Cobalt (wt%)	Tungsten (wt%)	Niobium (wt%)	Tantalum (wt%)	Titanium (wt%)	Aluminum (wt%)	Zirconium (wt%)	Boron (wt%)	Nickel (wt%)
Comparative sample #1	0.1	22.5	19	2	0.8	1	2.3	1.2	0.01	0.004	51.05
#2	0.1	22.5	19	2	1.35	0	2.3	1.7	0.01	0.004	51.03
#3	0.1	22.5	19	2	1.35	0	1.6	1.6	0.01	0.004	51.83
#4	0.1	22.5	19	2	1.35	0	1.95	1.4	0.01	0.004	51.68
#5	0.1	22.5	19	2	1.64	0	1.77	1.51	0.01	0.004	51.46

[0035] The results of the creep tests are shown in the figure, where the time taken to reach a strain of about 0.5% and 1% is compared for both samples. From the figure, it may be seen that there is a 200% improvement in creep displayed by the samples that are devoid of tantalum over the comparative sample, which as noted above, has tantalum. Similarly at a 1% strain the sample that is devoid of tantalum shows a 220% improvement in creep over the comparative composition.

[0036] A metallographic and image analysis performed on the Samples #2 – 6 shows that each of them had about the same amount of the  $\gamma$  phase, with very little of the undesirable  $\eta$  phase.

[0037] From the above example, it may be seen that the nickel-containing alloy that does not contain tantalum displays superior creep resistance properties over those that do, and hence may be advantageously used in high temperature applications such as in gas turbines and the like. The turbines comprising the nickel-containing alloys may be used in aircraft and spacecraft, land based power generation systems and craft that travel on and in water such as ships, submarines, barges, and the like.

[0038] While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

[0039] What is claimed is: